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PATENT SPECIFICATION

DRAWINGS ATTACHED



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COMPLETE SPECIFICATION

Process for Forming Surface Diffusion Alloys on Refractory Metal Members

We, OFFICE NATIONAL D'ETUDES ET DE RECHERCHES AEROSPAZIALES (par abréviation O.N.E.R.A.) a body corporate organized under the laws of France, 29 Avenue 5 de la Division Leclerc -92 Chatillon-sous-Bagneux, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates firstly to processes for the formation of surface diffusion alloys of chromium and aluminium, and 15 if appropriate of silicon also, on metal members which will be referred to in general as "refractory metal members" and whose qualitative composition will be stated more precisely hereinafter, and secondly to refractory metal members obtained by a said process according to the invention.

It is an object of the invention to adapt such methods and members more satisfactorily than hitherto to various practical requirements and more particularly to give the treated members increased resistance to corrosion, more particularly the corrosive action of high temperature combustion 30 gases.

Herein, the expression "refractory metal members" refers to members comprising an alloy having a base of iron, nickel or cobalt, or any combination of such metals, 35 the alloy being such that it has an ability to withstand mechanical stresses under heat, and also in general a degree of corrosion resistance at elevated temperatures, particularly when disposed in oxidising, oxidising-reducing, or sulphurated atmospheres, such, for instance, as those formed by the combustion gases of internal combustion engines.

In the present state of technology, alloys
[Price]

of the kind specified can be divided into four main categories, namely:

rust-resistant steels, for instance "INOX-IUM" steel (Fe 83, Cr17), 18-8 steel (Fe-74, Cr 18, Ni 8), and 25-20 steel (Fe 55, Cr 25, Ni 20);

refractory steels, for instance "NICK-RAL-D" (Cr 25, Ni 25, C 0.10 to 0.4 residue Fe);

refractory alloys having a nickel base, for instance,

"NIMONIC 75" (Cr 20, Ti 0.4, Al 0.06, Fe 2.4, C 0.10, residue nickel);

"NIMONIC 80" (Cr 20, Ti 2, Al 2, C 0.10, residue nickel);

"IN 100" (Cr 9.5, Mo 3, Co 15, Ti 5 C; 60 0.20, Al 5.5, W 1 residue nickel);

"INCONEL 713" (Co 10, Cr 13.5, Ti 2, Al 5.5 Mo 3, Ni 2.5, C 0.10, residue nickel);

"PWA 663" (Co 10, Cr 8, Ti 1, Mo 6, Ta 4.4, residue nickel);

"TD Nickel" (Ni 98, Th02-2);

and refractory alloys having a cobalt base, for instance "HS 25" or "L 605" (Cr 20, Ni 10, W 15, Fe 3, C 0.10, residue cobalt), "WI 52" (Cr 21, W 11, Nb and Ta 2, Fe 2, C 0.50, residue cobalt), and "SM 302" (Cr 21, W 10, Ta 9, Fe 1, C 0.85, residue cobalt). The words "NIMONIC" and "INCONEL" are Trade Marks.

It should be noted that the invention also applies to cases in which these refractory metal members have been given another surface metal diffusion treatment, more particularly a tantalum or chromium diffusion treatment.

The expression "magnesothermic chromium" herein means an ultra-fine powder of chromium obtained magnesothermically, processes for the preparation of such powders being disclosed, *inter alia*, in French Patent No. 1,123,326 and its Additions Nos. 70 936 and 79 879.

According to the invention there is pro-

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Fig.1.

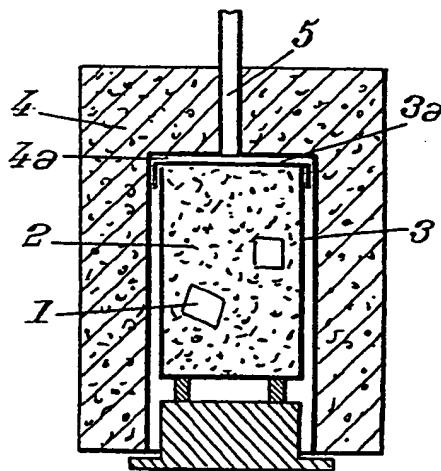
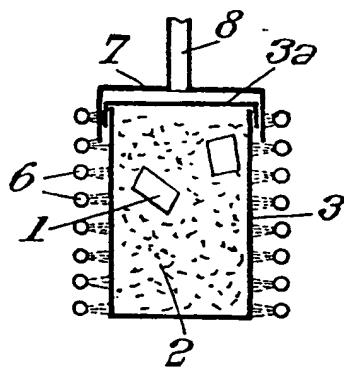


Fig.2.



also the chromium base alloy, contains silicon.

5. A process according to Claim 3, wherein the chromium base alloy contains from 3 to 10% by weight of silicon.

6. A process according to any one of Claims 1 to 4, wherein the halogenated constituent comprises a halogen, halogenide, hypohalogenite or mixture(s) thereof.

10 7. A process according to any one of the preceding claims, wherein the chemically inert diluting agent has a maximum mean grain size of 1 micron.

8. A process according to any one of 15 the preceding claims, wherein the chemically inert diluting agent is calcined alumina.

9. A process according to any one of 20 the preceding claims, wherein the reactive mass comprises from 5 to 50% by weight of the ultra-fine powder, from 0.05 to 1% by weight of the halogenated constituent, the balance comprising the chemically inert diluting agent.

25 10. A process according to any one of the preceding claims, wherein the temperature of heating is in the range of from 1050°C to 1100°C.

11. A process according to any one of 30 the preceding claims, wherein the reactive mass and the refractory metal member to be treated are contained in a casing during the heating.

12. A process according to any one of 35 the preceding claims, wherein the ultra-fine powder was prepared by heating an intimate mixture of magnesothermic chromium and aluminium powder at a temperature of from 750°C to 1200°C in an enclosed at 40 least partially gas-tight atmosphere which contains hydrogen, the chromium base alloy thus formed thereafter being cooled in a protective atmosphere.

13. A process according to any one of 45 the preceding claims, wherein the or each protective atmosphere is of substantially the same composition as the or each atmosphere which contains hydrogen.

14. A process according to any one of 50 the preceding claims, wherein the or each atmosphere which contains hydrogen comprises electrolytic hydrogen, a mixture of hydrogen and argon, or cracked ammonia.

15. A process according to any one of 55 the preceding claims, wherein during a series of successive treatment operations using a particular reactive mass, the aluminium removed from the reactive mass is replenished by adding aluminium powder to the reactive mass between each or several treatment operations, such addition of aluminium powder being from 0.5 to 1% by weight of the reactive mass, and wherein the chrom-

ium, being removed from the reactive mass being at a slower rate of removal than aluminium, is replenished by adding at intervals a quantity of ultra-fine chromium powder, which has a maximum mean grain size of 1 micron, in an amount of from 0.5 to 1% by weight of the reactive mass.

16. A process according to Claim 14, wherein addition of the chromium powder is effected after every four of five treatment operations with the reactive mass.

17. A process according to any one of 75 the preceding claims, which is applied to a refractory metal member which has already been given another surface diffusion metal treatment.

18. A process according to Claim 16, 80 wherein the said another surface diffusion metal treatment is a tantalum or chromium diffusion treatment.

19. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 1.

20. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 2.

21. A process for the formation of a 90 surface diffusion alloy, substantially as described in foregoing Example 3.

22. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 4.

23. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 5.

24. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 6.

25. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 7.

26. A process for the formation of a 105 surface diffusion alloy, substantially as described in foregoing Example 8.

27. A process for the formation of a surface diffusion alloy, substantially as described in foregoing Example 9.

110 28. A process for the formation of a surface diffusion alloy, substantially as hereinbefore described with reference to the accompanying drawing.

29. A surface diffusion alloy on a refractory metal member, whenever prepared by the process of any one of the preceding claims.

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in the form of fine powder having a maximum mean grain size of 1 micron (95% by weight), with the addition of 1% by weight of ammonium chloride. The whole 5 was heated for 6 hours at 1080°C in a protective hydrogen atmosphere. The treatment produced members having tantalum diffusion sheathings of a shiny appearance, which were plastic in both the cold and hot state 10 and had a regular thickness of about 35 microns.

The members thus tantalised were then subjected to a plastic chromaluminisation operation according to the invention for 8 15 hours at 1080°C, using a reactive body having the following mean composition: chromium 30%, aluminium 5%, alumina 65%, with the addition of 0.5% of ammonium chloride (a cement on the basis of ultra-fine magnesothermic chromium powder having a maximum mean grain size of 1 micron, finely powdered aluminium having a maximum mean grain size of 1 micron and an inert diluting agent comprising fine 20 25 calcined alumina having a maximum mean grain size of 1 micron the body having previously been homogenised during a "blank" operation.

The resulting members had a homogeneous semi-shiny surface appearance; the protective sheaths formed by the superimposition of two successive treatment were plastic in the cold state and had a regular thickness of about 50 microns. They gave 30 35 very effective protection to the treated members against the corrosive action of high temperature combustion gases, even with very violent thermal shocks.

EXAMPLE 9

40 *Chromaluminisation of members made of refractory alloy "INCONEL 713" and pre-sheathed by chromium diffusion.*

In this case the object of the preliminary chromium-diffusion sheathing treatment is 45 to ensure improved behaviour of the protected members in highly sulphurated combustion gases, and also to reduce the intergranular penetrations of aluminium which may occur in the surface zones of the members during the chromaluminisation treatment.

The preliminary chromising treatment was performed under conditions obviating the formation of surface zones made fragile as a result of excessive chromium enrichment. The members were chromised by 55 means of a treatment body using ultra-fine powders of nickel-chromium having a maximum mean grain size of 1 micron and produced by the preliminary heating of a 60 mixture of ultra-fine powder of chromium having a maximum mean grain size of 1 micron (25% by weight), fine nickel powder (10% by weight) having a maximum mean 65 grain size of 1 micron, fine calcined alu-

mina having a maximum mean grain size of 1 micron (65% by weight), with the addition of 1% by weight of ammonium chloride. The resulting reactive chromisation bodies are maintained between the various operations by the addition of 1% by weight of chromium powder and 0.5% of ammonium chloride or bromide. In the case considered here, the members are given a chromising treatment lasting six hours at 70 75 1050°C in a protective hydrogen atmosphere. The treatment produces smooth chromium diffusion sheathings which have a homogeneous semi-shiny appearance, and are plastic in the cold state because of their 80 limited chromium content, the sheathings have a regular thickness of about 35 microns.

The members thus chromised are then given a further plastic chromaluminisation 85 treatment in the same conditions as those described in the preceding Example. The members then have a homogeneous semi-shiny surface appearance and are sheathed in alloys which are rich in both chromium 90 and aluminium and whose total thickness is about 65 microns. The sheathings are plastic in the cold and hot state and protect the members very satisfactorily up to about 1050°C in combustion gases of fuels whose 95 sulphur content can be as high as 3-4%.

WHAT WE CLAIM IS:—

1. A process for the formation of a surface diffusion alloy of chromium and aluminium on a refractory metal member, 100 which process comprises the steps of:—
a) contacting the surface of the refractory member to be treated with a reactive mass comprising an intimate mixture of (1) an ultra-fine powder having a maximum 105 mean grain size of 1 micron, the grains of the ultra-fine powder being formed of a chromium base alloy which contains aluminium, (2) an oxide powder which is stable throughout the process present as a chemically inert diluting agent and (3) a liquid or solid halogenated constituent;
b) heating the reactive mass in contact with the surface of the refractory metal member to be treated in an atmosphere 110 which contains hydrogen, the temperature of heating being from 750°C to 1200°C, and;
c) after step (b) cooling the reactive mass and the refractory metal member in 115 a protective atmosphere.

2. A process according to Claim 1, wherein the atmosphere which contains hydrogen is present in a partially gas-tight enclosure.

3. A process according to Claim 1, wherein the chromium base alloy contains from 5 to 25% by weight of aluminium.

4. A process according to Claim 1 or 2, wherein the surface diffusion alloy, and 120 125 130

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nisation treatment to these materials allowed a reduction of the scaling rates by more than 95% against those of members subjected to the tests without preliminary protection.

EXAMPLE 5

Protection of distributor bladings with carborised refractory alloys on "WI 52" cobalt base.

10 The members to be protected were treated according to the invention for 10 hours at a temperature of 1050°C. After treatment, the members had a very smooth surface condition and a light orange beige appearance. The thickness of the diffusion sheathings obtained reached about 45 microns, the sheathings being free from all porosity, inclusions or cracks and insensitive to the action of the most violent mechanical or thermal shocks.

Corrosion-resistance tests in high temperature combustion gases, similar to the tests described in Example 1, showed that the application of the plastic chromaluminisation treatment allowed the scaling rates to be reduced by more than 97% as against those normally observed in members subjected to the tests without preliminary protection.

EXAMPLE 6

Protection of Combustion chambers formed by brazed assemblies of rust-resistant steel "18/8", "NIMONIC 75" and "HS 25".

35 The members were formed by assembled of 18/8 (bases), "NIMONIC 75" (actual combustion chambers) and "HS 25" (flame tubes) which had first of all been brazed *in vacuo* by means of nickel-chromium-boron-silicon brazings.

The members to be protected were treated according to the invention for 15 hours at 980°C. After treatment, the thickness of the diffusion sheathings reached 120 microns on the parts made up of "18/8" rust-resistant steel, 50 microns on the parts made up of "NIMONIC 75" and 40 microns on the parts made of "HS 25", the sheathings being in all cases free from any inclusions, porosity or cracks, and fully plastic in the cold or hot state.

During tests at the bench, and practical tests carried out on engines under very severe conditions, no failure was observed in the sheathings, even when highly sulphurated fuels were used, the scaling rates of the members treated remaining in all cases practically negligible.

EXAMPLE 7

Protection of movable fins made of "INCONEL 713" and previously sheathed by tantalum diffusion.

Before the application of the chromaluminisation treatment according to the invention, the fins were sheathed by tantalum

diffusion, the tantalisation treatment allowing a substantial improvement in the flow behaviour characteristics of the materials treated.

To perform the preliminary tantalisation treatment, the members were heated for 4½ hours at 1080°C in partially gas tight casings in a hydrogenated protective atmosphere, the members being immersed in pulverulent mixture of (1) an inert diluting agent comprising fine calcinated alumina having a maximum mean grain size of 1 micron (97.5% by weight) and (2) very fine tantalum powder having a maximum mean grain size of 1 micron (2.5% by weight), with the addition of 0.5% by weight of ammonia chloride.

This preliminary treatment produced diffusion sheathings very rich in tantalum and having a thickness of 30 microns with deeper preferential penetrations of the tantalum in accordance with the joints between the grains of material.

The pre-tantalised fins of "INCONEL 713" were first treated according to the invention in a pre-homogenised chromaluminisation body to which 5% of silicon had been added, the protection treatment being performed for 8 hours at a temperature of 1080°C.

After the protective treatment by the simultaneous diffusion of aluminium, chromium and silicon, the members had a very smooth surface condition and a highly homogeneous semi-shiny sky blue appearance. The protective sheathings obtained had a thickness of about 55-60 microns and were free from all porosity, cracks or inclusions and fully plastic, even in the cold state. They gave very satisfactory protection for very long periods to the members treated against the action of combustion gases up to temperatures as high as 1100°C.

EXAMPLE 8
Chromaluminisation of members made of "T.D. Nickel", pre-sheathed by tantalum diffusion.

Experimental turbine rotors to be protected by plastic chromaluminisation, were first of all given a tantalum-diffusion sheathing treatment. The preliminary treatment was intended to prevent the aluminium from rediffusing too deeply during the utilisation of the protected members; it was also aimed at preventing reaction between the thorium of the "T.D. Nickel" and the aluminium supported in the nascent state during the chromaluminisation treatment.

The preliminary tantalisation treatment was performed by bringing the members into contact in partially gas-tight nickel casings with an intimate mixture of tantalum in the form of very fine powder having a maximum mean grain size of 1 micron (5% by weight) and calcined alumina

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If the materials to be treated are strongly carbonised, it is advantageous to add to the reactive mass, in addition to the ammonium chloride (or bromide) 0.5-1% by weight of a compound such as aluminium fluoride (AlF_3 ; 0.5 H_2O or AlF_3 ; 3.5 H_2O), this compound acting as a surface decarbonising agent at the start of the operation.

The following Examples illustrate the invention. The above reactive mass is used in Examples 1 to 7, and the chromium aluminium alloy is formed *in situ* by a preliminary so-called "blank" operation performed at 1000°C for about an hour, observing the other conditions laid down for the chromaluminisation treatment.

EXAMPLE 1

Protection of moving vanes of turbines

The members to be protected were made of "INCONEL 713" refractory alloy and were given a thermal treatment according to the invention for six hours at a temperature of 1080°C. After the treatment the members had a very smooth surface condition and a highly homogeneous sky blue semi-shiny appearance. The thickness of the diffusion sheaths obtained reached about 65 microns. The protective sheaths were rich in chromium and aluminium and free from all porosity, inclusions or cracks; they were clearly plastic even in the cold condition, whatever rate of deformation was applied to the members, and they were moreover completely insensitive to the action of the most violent thermal or mechanical shocks.

Anti-corrosion tests, for resistance to corrosion, lasting for 300 hours at 1100°C with interposed thermal shocks, even in strongly sulphurated combustion gases, showed that the scaling rates, which were determined at the end of the tests, were practically negligible (below 2 mg/cm^2 , whereas the same members subjected to the anti-corrosion test without preliminary protection were seriously damaged and had scaling rates reaching about 30-40 mg/cm^2 .

Substantially equivalent results as regards the appearance of the members, the homogeneity and plasticity of the sheaths and resistance to corrosion and thermal shocks, were obtained by treating, under the same conditions, members made of different nickel-base refractory alloys: "SM 200", "UDIMET 700", "P.W.A. 663", "IN 100", "T.D. Nickel" . . . The word "UDIMET" is a Trade Mark.

In this case also, the scaling rates observed during the anti-corrosion test in high temperature combustion gases were always practically negligible, while the scaling rates in the same materials without preliminary protection were generally very high and in some cases ("T.D. Nickel", "IN

100") amounted to complete destruction of the members.

EXAMPLE 2

In this example the members to be protected were identical to those in Example 1, and the treatment was performed, according to the invention, in an operation lasting for 20 hours at 900°C.

The surface appearance of the members, homogeneity of diffused sheaths, plasticity in the cold state or at elevated temperature and lack of sensitivity to thermal shocks were similar to the characteristics described in Example 1, but the thickness of the diffusion sheathings obtained was lower, being between approximately 25 and 35 microns, in dependence on the nature of the materials treated.

EXAMPLE 3

In this example, the treatment conditions used and the materials treated were identical to those in Example 1, except that chromaluminisation reserves were prepared at the bases of the vanes. To this end, the vane bases were first of all covered with several thicknesses of iron or nickel sheet and placed in bowls containing powdered calcined alumina, with the addition, if necessary, of iron powder or nickel powder. The bowls containing the alumina were machined so as to fit almost exactly into the top rectangular portion of the vane bases.

The thickness of the sheathings obtained on surfaces not furnished with reserves was not affected by the modification made to the conditions under which the treatment was performed; as against this, the vane bases provided with reserves were substantially not chromoluminised.

EXAMPLE 4

Protection of distributor blading by refractory alloy on "HS25" cobalt base.

The members to be protected were treated according to the invention for 8 hours at a temperature of 1080°C. After treatment, the member had a very smooth surface condition and a highly homogeneous semi-shiny light orange beige appearance. The thickness of the diffusion sheathings obtained reached about 55 microns. The protective sheathings were rich in chromium and aluminium and free from all porosity, inclusions or cracks; they were completely plastic, even in the cold condition, whatever the deformation rates applied, and were completely insensitive to the action of the most violent mechanical shocks.

Corrosion-resistance tests in high temperature combustion gases, similar to the tests described in Example 1, showed that the application of the plastic chromalumi-

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rated by cross-members which enable the reaction masses to be heated more quickly and uniformly.

Figure 2 illustrates the cooling stage of 5 the casing 3 and its charge, after the thermal treatment has been performed, cooling being produced by water-spraying banks 6 after the casing 3 has been quickly transported under a protective cover 7 supplied 10 with a protective atmosphere containing hydrogen via a conduit 8, a pressure drop produced in the casing 3, as a result of the cooling of the casing and its contents encouraging the entry of the protective atmosphere into the casing.

At this point it should be stressed that in the chromaluminisation process according to the invention, the ultra-fine nature of the metallic constituent of the reactive 20 mass (powder of an alloy having a maximum mean grain size of 1 micron) is of primary importance. This ultra-fine grain size of the alloy powder not only provides a large extent of surface, which clearly encourages the exchange reactions, but also has a further important advantage in the case under consideration, in which the alloy powder contains aluminium, since aluminium transported from the surface layer of 30 each grain of alloy powder to the surface of the member to be treated has a tendency to diffuse more rapidly in the crystalline lattice of the member treated than in the crystalline lattice of the particular grain.

35 The result is a reduction in the concentration of aluminium in the surface layer of the alloy grains by a compensating effect, this reduction in the concentration causes a migration of the aluminium atoms 40 from the centre of the grains of alloy towards their surfaces. The rate at which the concentration of aluminium in the surface layer is restored, by the migration of aluminium atoms from the centre of the grains, 45 depends upon the distance which the migrating atoms must traverse. Clearly, therefore, in the process according to the invention the ultra-fine nature of the alloy powder is very important, since the surface 50 layer of each grain can be rapidly regenerated with aluminium from the centre of the grain, because of the very small distance over which the atoms have to migrate, and this has the effect of keeping the ratio of 55 the quantities of aluminium and chromium in the alloy deposited substantially constant.

The preferential transference of aluminium to the surface of the refractory member treated (since that metal has a higher 60 positivity) can be readily compensated by adding a little aluminium powder to the reactive mass between each treatment operation, the addition of aluminium powder being, for example, 0.5 - 1% by weight of 65 the reactive mass. The gradual but slower exhaustion of the chromium in the reactive

mass can be compensated by occasionally adding thereto (for instance every four or five operations) chromium in the form of an ultra-fine powder having a maximum 70 mean grain size of 1 micron and again in a ratio of 0.5-1% by weight of the reactive mass.

The ultra-fine grain size of the metallic constituent of the reactive body implies a 75 fine grain size in the constituent acting as a chemically inert diluting agent. The fine grain size is preferably of the order of 1 micron but this is not absolutely necessary, the fineness of grain size of the constituent 80 acting as an inert diluting agent being less essential than that of the metallic constituent. If the grain size of the inert diluting agent is too large, grains of the alloy powder will be able to form an agglomerate in 85 the interstices between the grains of the inert diluting agent and thus the inert diluting agent will not satisfactorily fulfil its function. Thus, an inert diluting agent can be used which has a grain size smaller than 90 1 micron or larger than 1 micron, but in the latter case the proportion of inert diluting agent should be greater.

It has been found that the weight ratio between the inert diluting agent and the 95 metal constituent of the reactive body is not critical, and the ratio may in practice vary from 1 to 20.

In addition to the advantages already 100 stated, the chromaluminisation process according to the invention may have the following further advantages:

the members treated have a hermetic sheathing which is free from porosity and cracks, an outstanding surface quality, plastic surface layers in both the cold and the hot states (such plasticity giving the members an exceptionally high resistance to thermal shocks), and an increased chromium content in the surface layers such that 110 they have improved corrosion resistance in combustion gases containing sulphur;

the reactive masses used do not "age", do not suffer any inhibition (their nitrogen content can safely reach considerable values) 115 so that the masses can be used for a practically unlimited period, and never contain fragile inter-metallic compounds of chromium-aluminijum.

A number of examples will now be given 120 of the application of the chromaluminisation process, according to the invention, to various refractory alloys, the reactive mass used in the examples having the following composition, which is by way of example 125 only.

Magnesothermic

chromium	40% by weight
Aluminium	10% by weight
Fine calcined alumina	49.2% by weight
Ammonium chloride (or bromide)	0.8% by weight

vided a process for the formation of a surface diffusion alloy of chromium and aluminium on a refractory metal member, which process comprising the steps of:—

5 a) contacting the surface of the refractory member to be treated with a reactive mass comprising an intimate mixture of (1) an ultra-fine powder having a maximum mean grain size of one micron, the grains 10 of the ultra-fine powder being formed of a chromium base alloy which contains aluminium, (2) an oxide powder which is stable throughout the process present as a chemically inert diluting agent, and (3) a liquid 15 or solid halogenated constituent;

b) heating the reactive mass, in contact with the surface of the refractory metal member to be treated in an atmosphere which contains hydrogen, the temperature 20 of heating being from 750°C to 1200°C, and

c) after step (b) cooling the reactive mass and the refractory metal member in a protective atmosphere.

25 Thus the member to be treated may, for example, be treated by bringing the whole of its surface into contact with a reactive mass comprising in intimate mixture three main constituents — i.e., firstly:— a metal 30 constituent in the form of an ultra-fine powder, having therefore a large amount of surface, and a mean grain size equal to 1 micron or less, each grain being formed by a chromium-base alloy which contains aluminium 35 in a proportion of 5-25% by weight of the alloy and if appropriate silicon, in a proportion of 3-10% by weight of the alloy, the alloy powder being formed either *in situ* by a preliminary thermal treatment 40 preceding the introduction of the member into the reactive body, or in some other place during an operation completely independent of the chromaluminisation treatment, the formation of the alloy powder 45 being preferably performed *in situ* from magnesothermic chromium and very fine aluminium powder formed by particles at least one of the dimensions of which is at most equal to 1 micron; secondly, a constituent 50 acting as a chemically inert diluting agent and taking the form of a fine powder having a mean grain size of about 1 micron and formed by an oxide which is stable throughout the process e.g. calcined alumina, and thirdly a liquid or solid halogenated constituent (halogen, halogenide, hypohalogenite, or mixtures thereof) the proportions by weight of the three kinds of constituents being preferably 5-50% for 55 the metal constituent, 0.05-1% by weight for the halogenated constituent, the residue being the constituent acting as an inert diluting agent;

60 the reactive mass and the member to be treated disposed within the reactive mass,

are then placed in a partially gas-tight casing which permits only a limited flow of gas therein and which is disposed in a heating enclosure in which there is an at least partially hydrogenated protective atmosphere which can be formed *inter alia* by ordinary electrolytic hydrogen, a mixture of hydrogen and argon, or cracked ammonia;

65 heating is then performed, during which the heating enclosure is kept at a temperature of between 750 and 1200°C, preferably between 1050 and 1100°C, the temperature and duration of the heating being selected *inter alia* in relation to the required thickness of the layer of diffusion alloy; and lastly the partially gas-tight casing is cooled in a protective atmosphere which 75 can be the same as that used during the heating.

80 The reactive mass may be formed either *in situ* by a preliminary thermal treatment prior to bringing the surface of the refractory member into contact with the reactive mass, or in an operation completely independent of the chromaluminisation treatment and for the preparation of the reactive mass it is preferable to use magnesothermic chromium powder having a maximum mean grain size of one micron and very fine aluminium powder formed by particles at least one of the dimensions of which is at most equal to one micron.

85 Apart from the main feature set forth hereinbefore, the invention comprises certain other desirable though not essential features which are preferably used simultaneously and will be described in greater detail hereinafter.

90 For a better understanding of the invention reference will now be made, by way of example, to the accompanying drawing, in which:—

95 FIGURES 1 and 2 diagrammatically illustrate an apparatus for the performance of the process according to the invention;

100 FIGURE 1 corresponding to the chromaluminisation thermal treatment properly so called, while:

105 FIGURE 2 corresponds to a cooling operation following the aforementioned thermal treatment.

110 Referring to the drawing, Figure 1 shows a chromaluminisation apparatus according to the invention, members 1 to be treated being immersed in a reaction mass 2 contained in a steel casing 3 having a partially gas-tight cover 3a and disposed in an enclosure 4a of a bell-shaped furnace 4, a protective atmosphere containing hydrogen 115 being supplied to the enclosure 4a via a conduit 5. Advantageously, a number of independent treatment casings 3 are disposed simultaneously in the enclosure 4a, and the casings 3 are advantageously sepa- 120

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